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(54) LAMINATE, RESIN OR RESIN COMPOSITION FOR FORMING LAMINATE AND METHOD FOR TREATING THE LAMINATE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a packing laminate advantageous in economy by improving a working environment with satisfactory heat sealability and low odor, securing safety and reducing number of steps.

SOLUTION: The laminate comprises a base material layer which is not anchor-coated and ethylene-α-olefin copolymer resin in such a manner that adhesive strength of the laminate is 300 g/15 mm width or more. In the laminate forming resin composition for forming the laminate by extrusion laminating at least one side surface of the layer, the laminate forming resin or resin composition has MFR of 1 to 100 g/10 min, a density of 0. 900 g/cm or lower and relationship between an extraplation melting finishing temperature(Tem) of a melting peak and the density satisfying a relational formula of tem≤286D-137. And the laminate is

heat treated at 40°C or higher.

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MEANS

[Means for Solving the Problem] As a result of repeating research wholeheartedly in view of the above-mentioned trouble, even if this invention person low-temperature-izes the extrusion temperature of thermoplastics by using the resin of a character [****], he used to come to complete this invention based on knowledge that the layered product from which anchor-coat processing was not performed but which ** also excelled in the bond strength of a base-material layer and a glue line is obtained. That is, the layered product of this invention is a layered product which consists of a resin constituent layer containing the base-material layer, the ethylene and the alpha olefin copolymer resin, or this copolymer resin to which anchor-coat processing is not performed, and is characterized by the bond strength of this layered product being more than 300g/15mm width of face. Moreover, the resin for layered product formation or resin constituent which is another invention of this invention In the resin for layered product formation or resin constituent for carrying out an extrusion lamination and forming a layered product at least in one side of a base-material layer to which anchor-coat processing is not performed This resin for layered product formation or a resin constituent is 1-100g of MFRs, and 10 minutes, and it is density 0.900 g/cm3. Relation between the extrapolation dissolution end temperature (Tem) of a dissolution peak and density is hereafter characterized by being what fills the following relational expression.
Tem<=286D-137 -- after the art of the layered product which is another invention of this invention carries out the extrusion lamination of the resin constituent which contains ethylene and the alpha olefin copolymer resin, or this copolymer resin at least on one side of the base-

material film with which anchor-coat processing is not performed and considers as a layered product, it is characterized by heating this layered product at the temperature of 40 degrees C or more again

[0006]

[Embodiments of the Invention]

[I] Layered product (1) The bond strength of the base-material layer and glue line to which the layered product of a lamination this invention carries out the laminating of the glue line which turns into a base-material layer to which anchor-coat processing is not performed from ethylene and the alpha olefin copolymer resin, and the aforementioned anchor-coat processing is not performed is the thing of 300 - 500g/15mm width of face preferably more than 300g/15mm width of face.

[0007] (i) As a material used for the base-material layer of the layered product of a base-material layer this invention, metallic foils, such as un-extending or the oriented film of synthetic resin, such as polyamide resin, such as polyester resin, such as polyolefin resin, a saponification object of an ethylene vinylacetate copolymer, polystyrene resin, and a polyethylene terephthalate (PET), and nylon, a polyvinyl alcohol resin, a polyvinyl chloride resin, and a polyvinylidene chloride resin, a sheet or aluminum, iron, and copper, or a metal plate, textile fabrics or a nonwoven fabric, paper, cellophane, etc. can be mentioned It is desirable to use polyamide resin, such as polyester, such as a polyethylene terephthalate (PET), and a nylon oriented film (ONY), a polypropylene oriented film (OPP), and a metallic foil also in these. Generally as for the above-mentioned base-material layer, 7-200 micrometers of things with a thickness of 7-50 micrometers are used preferably. These can also perform a corona treatment, frame processing, ozonization, etc. for the front face if needed.

[0008] (ii) It is the resin constituent which contains the copolymer resin obtained from ethylene and an alpha olefin (alpha olefin which is the molecule skeleton of 3-10 carbon numbers especially preferably 3-18 carbon numbers preferably), or this copolymer resin as the ethylene and alpha olefin copolymer resin used as a glue line of the layered product of a glue-line this invention. It is the resin constituent which specifically contains the copolymer resin obtained from one sort of the alpha olefin of ethylene, butene-1 and a hexene -1, an octene -1, and 4-methyl pentene-1 grade, or two sorts or more of mixture, or this copolymer resin. Generally as for the above-mentioned glue line, 10-100 micrometers of things with a thickness of 15-50 micrometers are used preferably.

[0009] (iii) Other layers (arbitrary layer)

An arbitrary layer can be formed in addition to the base-material layer in the layered product of this invention, and the indispensable layer of a glue line. As a material used for this arbitrary layer, polyolefine system resins, such as polyethylene system resins, such as a high-pressure-produced-polyethylene resin and an ethylene-vinylacetate-copolymer resin, and a polypropylene regin, etc. can be mentioned. Generally as for the above-mentioned arbitrary layer, 1-100 micrometers of things with a thickness of 10-50 micrometers are used preferably.

[0010] [II] Ethylene and alpha olefin copolymer resin constituent (1) Ethylene and alpha olefin copolymer resin (component A)

(a) Object As for the sex above-mentioned ethylene and an alpha olefin copolymer resin, it is desirable to use what shows the following physical properties.

** 1-100g / thing that shows 3-50g / 10 minutes preferably is used for MFR (melt flow rate : melting flow rate) according [the ethylene and the alpha olefin copolymer resin used in an MFR this invention] to JIS-K7210 for 10 minutes. Adhesion with a base-material layer will become it small that this MFR is under the above-mentioned range, and the spread nature of a resin will be lost. Moreover, if this MFR exceeds the above-mentioned range, the neck in will be large and a melting thin film with the uniform case of a gap will not be obtained.

[0011] ** Dense For the ethylene and the alpha olefin copolymer resin used in a degree this

, invention, the density (D) by JIS-K7112 is 0.900 g/cm3. They are 0.895 g/cm3 preferably hereafter. It is 0.890 - 0.865 g/) especially preferably hereafter. What hown is used. If this density is larger than the above-mentioned range, an adhesive property with a base-material layer will become small, and a layered product with strong intensity will not be obtained.

[0012] ** Extrapolation dissolution end temperature of the dissolution peak by the differential scanning calorimetry (DSC) (Tem)

The line which extended the base line by the side of the elevated temperature of the DSC curve by which the ethylene and the alpha olefin copolymer resin used in this invention were measured based on JIS-7121 to the low temperature side, The relation of the extrapolation dissolution end temperature (Tem) and density (D) which are the temperature of an intersection with the tangent drawn in that the inclination of the curve by the side of the elevated temperature of a dissolution peak serves as the maximum Tem<=286D-137 -- they are Tem<=349D-197 and the thing which satisfies the relational expression of Tem<=429D-271 most preferably preferably

[0013] (b) manufacture of ethylene and the alpha olefin copolymer resin -- although such ethylene and alpha olefin copolymer resin may be the thing manufactured using the metallocene system catalyst shown below and the thing manufactured using the conventional vanadium system catalyst, and ********, what was manufactured using the metallocene catalyst is desirable

[0014] As a resin manufactured using the resin metallocene catalyst manufactured using the metallocene catalyst JP,58-19309,A, JP,59-95292,A, JP,60-35005,A, JP,60-35006,A, JP,60-35007,A, JP,60-35008,A, Each official report of JP,60-35009,A, JP,61-130314,A, and JP,3-163088,A, The European Patent application public presentation No. 420,436 specification, a U.S. Pat. No. 5,055,438 specification, And the method indicated by the international public presentation official report WO 91/No. 04257 specification etc., i.e., a metallocene catalyst, a metallocene/alumoxane catalyst, Or the catalyst which consists of a compound which reacts with a metallocene compound and a metallocene catalyst which are indicated by the international public presentation official report WO 92/No. 07123 specification etc., for example, and serves as stable ion is used. Copolymerization of the ethylene of a principal component and the alpha olefin of an accessory constituent is carried out, and they are manufactured.

[0015] As a resin manufactured using the resin vanadium system catalyst manufactured using the vanadium system catalyst, depending on the method indicated by JP,52-39741,A, i.e., a vanadium compound and an organoaluminium compound, and the case, further, the catalyst which comes to add a third component is used and it is manufactured by copolymerizing the ethylene of a principal component, and the alpha olefin of an accessory constituent.

[0016] (2) Combination resinous principle (component B)

Although the above-mentioned ethylene and alpha olefin copolymer resin (component A) can also be used independently, it is desirable to use the ethylene and the alpha olefin copolymer resin content constituent which blended with this ethylene and alpha olefin copolymer resin combination resinous principles (component B), such as a resin which can raise the low-density-polyethylene resin for an extrusion lamination and/or extrusion lamination aptitude. It is desirable to use the low-density-polyethylene resin for an extrusion lamination also in these.

[0017] (i) What shows the following physical properties as a low-density-polyethylene resin for the low-density-polyethylene resin above-mentioned extrusion lamination for an extrusion lamination is suitable.

** As a low-density-polyethylene resin used in the ethylene and the alpha olefin copolymer resin constituent of an MFR this invention, 1-50g / thing that shows the physical properties for 3-20g / 10 minutes preferably is used for MFR (melt flow rate : melting flow rate) by JIS-

K7210 for 10 minutes. If the spread nature of a resin is lost as this MFR is under the above-mentioned range, and this MFR exceeds the above-mentioned range, the neck in will be large and a melting thin film with the uniform case of a gap will not be obtained.

[0018] ** dense the density according to JIS-K7112 as a low-density-polyethylene resin used in the ethylene and the alpha olefin copolymer-resin constituent of a degree this invention -- 0.915 - 0.930 g/cm3 -- desirable -- 0.918-0.925g/cm3 What is shown is used. If this density is larger than the above-mentioned range, an adhesive property with a base material will become small, and a layered product with strong intensity will not be obtained.

[0019] (3) As the ethylene and alpha olefin copolymer resin (component A) contained in the blending-ratio-of-coal above-mentioned ethylene and an alpha olefin copolymer-resin constituent, it is especially used preferably 30 to 100% of the weight at least 20% of the weight by 40 - 80% of the weight of the blending ratio of coal. The combination resinous principle (component B) added in ethylene and an alpha olefin copolymer-resin constituent is especially used preferably ten to 70% of the weight 80 or less % of the weight by 20 - 60% of the weight of the blending ratio of coal. If there are not much too many loadings of the combination resinous principle (component B) added in the above-mentioned ethylene and alpha olefin copolymer-resin constituent, an adhesive property with a base-material layer will become small conversely. On the other hand, when there were too few loadings of the combination resinous principle (component B) added in ethylene and an alpha olefin copolymer-resin constituent and extrusion lamination is carried out by the monolayer, a neck in becomes large, and a uniform melting thin film is not obtained.

[0020] (4) Other combination components (arbitrary component)

Inorganic bulking agents, such as additives, such as a slipping agent, an antistatic agent, an antifogger, an ultraviolet ray absorbent, and an antioxidant, and a calcium carbonate, a silica, titanium oxide, talc, a pigment, etc. can be added to the grade which does not bar an adhesive property with a base-material layer to the resin constituent which blended the combination resinous principle (component B) with the above-mentioned ethylene and alpha olefin copolymer resin (component A), or this copolymer resin (component A).

[0021] [III] Manufacture of a layered product (1) As a method of manufacturing the layered product of the laminating method this invention, although various methods are employable, it is desirable to adopt the method of ** - ** shown below.

** Carry out the extrusion lamination of ethylene and the alpha olefin copolymer resin on the base-material film with which it is not given to anchor-coat processing, and obtain a layered product.

** On the base-material film with which it is not given to anchor-coat processing, carry out an extrusion lamination, carry out the laminating of ethylene and the alpha olefin copolymer resin, subsequently to an ethylene and alpha olefin copolymer-resin layer top, carry out the extrusion lamination of other resins, and obtain a layered product.

** Carry out the sandwiches extrusion lamination of ethylene and the alpha olefin copolymer resin between the base-material layer which is not given to anchor-coat processing and other resin film layers, and obtain a layered product.

** On the base-material film with which ethylene and the alpha olefin copolymer resin, and the good resin of extrusion lamination fitness are not given to anchor-coat processing, carry out a co-extrusion lamination in the state of the laminating which made the aforementioned ethylene and alpha olefin copolymer resin the base-material side, and obtain a layered product.

In addition, in order to carry out the extrusion lamination of ethylene and the alpha olefin copolymer resin by the monolayer in the above-mentioned ** - ** and to raise the extrusion lamination fitness of the aforementioned ethylene and alpha olefin copolymer resin, it is desirable to consider as the ethylene and the alpha olefin copolymer-resin constituent which added the low-density-polyethylene resin for an extrusion lamination or the resin which can,

in addition to this, raise the above-mentioned extrusion lamination fitness.
[0022] (2) Laminating condition) Generally as resin temperature at the : of carrying out an extrusion lamination and carrying out the laminating of laminating temperature ethylene and the alpha olefin copolymer resin, 150-320 degrees C is preferably performed at 200-300 degrees C. This resin temperature becomes poor [the spread nature of a resin] under at the above-mentioned temperature requirement, and a melting film becomes inadequate [a bond strength with about / not being obtained smoothly / and a base-material layer]. On the other hand, if resin temperature exceeds the above-mentioned temperature requirement, while problems, such as a fall of the heat-sealing nature as a laminated material and generating of an odor, will arise, a gel object is generated and problems, such as a fall of a mechanical strength and appearance, occur. In addition, it is important for a base-material layer to carry out a sticking-by-pressure lamination, using [190-320 degrees C is 200-300 degrees C still more preferably preferably, and extrude ethylene and the alpha olefin copolymer resin, and] a processing side as an adhesion side subsequently, from an adhesive property with a base-material layer, and a viewpoint of an odor, after ozonizing a melting film, a melting film, nothing, and.
[0023] (ii) Meat When forming ethylene and the alpha olefin copolymer resin by the monolayer and fabricating the thickness of the coat layer at the time of carrying out a thick extrusion lamination by 10-40 micrometers and co-extrusion generally, it is a 3-35-micrometer melting film. As for air GIAPPU of a laminator, it is common to usually be carried out by 100-150mm. Moreover, about lamination speed, it is desirable to be carried out by part for 80-150m/generally from a viewpoint of productivity.
[0024] [IV] The layered product of the heat treatment this invention of a layered product can strengthen a bond strength further by heat-treating 40 degrees C or more, after carrying out the laminating of film-like a base-material layer and a glue line. The processing under the atmosphere in which this heat treatment was contacted to the heated roll, the inside of oven was passed, or ** was heated is adopted. Less than 40 degrees C of a treatment effect of the temperature of this heat treatment are not enough, and a bond strength does not improve. This heat treatment is performed by being usually 100-150m speed for /about the inside of the heat-treatment process in the inside of the contact or the oven to a roll, and generally, usually processing a layered product for 2 - 3 seconds.

EXAMPLE

[Example] this invention does not have the range restrained by the following examples and examples of comparison, although an example and the example of comparison are indicated below and this invention is explained to it still more concretely, unless the summary is exceeded.
[I] The measurement of physical properties and the evaluation of film physical properties in the evaluation method example and the example of comparison were carried out by the method shown below.
[0026] (1) Measuring method of physical properties (A) It is based on MFR:JIS-K7210 (190 degrees C, 2.16kg load).
(B) Dense Degree: It is conformity (C) to JIS-K7112. Extrapolation dissolution end temperature by the differential scanning calorimetry (DSC) (Tem): Heat press. After carrying out weighing capacity of about 5mg sample from the fabricated 100-micrometer film, setting it in the DSC equipment made from SEIKO Electronic industry (RDC 220), carrying out a

temperature up to 170 degrees C and holding for 5 minutes at the temperature, it cools to -10 degrees C by part for 10-degree in temperature fall speed. After holding for 1 minute in the state, it measured by carrying out a temperature up to the temperature of 170 degrees C by part for 10 degrees-C/of programming rates. And the DSC curve when carrying out a temperature up even to 170 degrees C from -10 degrees C was obtained. Next, based on JIS-K7121, temperature of the intersection of the line which extended the base line by the side of the elevated temperature of a DSC curve to the low temperature side, and the tangent drawn in that inclination becomes the maximum at the curve by the side of the elevated temperature of a dissolution peak was made into extrapolation melting end temperature (Tem).

[0027] (2) The physical-properties evaluation method of a laminate film (A) Bond strength: After continuing beforehand the test piece with a width of face [of 15mm], and a length of 90mm in the 40mm of the length directions and exfoliating a base-material layer and a lamination layer, the maximum (g/15mm) when exfoliating T type in a part for 300mm/of speeds of testing with a SHOPPA type tension tester was measured.

[0028] (B) Heat-sealing intensity : two laminate films judged in width of face of 15mm were made to pile up mutually so that a lamination layer comrade may touch, it heat sealed in the heating-plate formula heat sealer in the seal temperature of 140 degrees C, pressure 2 kgf/cm2, and time 1 second, and the maximum (g/15mm) when exfoliating the obtained sample T type in a part for 300mm/of speeds of testing with a SHIWOPPA type tension tester was measured.

[0029] (C) After having made it meet so that the lamination layer comrade of a shock-resistant on-the-strength laminate film may lap, heat sealing the three way type in the heating-plate formula heat sealer (seal width of face of 0.5mm, the seal temperature of 140 degrees C, pressure 2 kgf/cm2, time 1 second), producing the 150mmx150mm bag body and being filled up with 200 cc water into it, it remained while heat sealed similarly. And it fell so that it might be mostly in charge of parallel in a griddle with a weight [of a size equivalent to it on the bag body] of 1kg, and the fall height (cm) of the griddle which the seal section of a bag body destroys by one fall was measured.

[0030] [II] it blended with the corona-treatment side of an ONY base-material (nylon oriented film : emblem ONM[by Unitika, Ltd.] # 15 15 micrometers) layer where an example, the example examples 1-7 of comparison and the example 1 of comparison - 2 anchor-coat processing are not performed from the T die of a co-extrusion laminator by the blending ratio of coal shown in Table 1 at a base-material side -- carry out melting mixture Ethylene and 10 micrometers of alpha olefin copolymer-resin constituent layers which fabricated the pelletized resin at the resin temperature of 290 degrees C in the shape of a film It co-extrudes so that it may become 30 micrometers of high-pressure-produced-polyethylene resin (LC600made from Japanese PORIKEMU C, MFR:190-degree C 7, and density 0.919 g/cm3) layers at the opposite side, and it makes with a melting film. subsequently From the nozzle installed in the position of 30mm under the die towards the ethylene and the alpha olefin copolymer-resin side of this melting film Ozone level 12 g/m3 After spraying and ozonizing air in a 1.5m3/o'clock amount, it has arranged so that the ozonization side of this ethylene and alpha olefin copolymer resin may lap with the corona-treatment side of a base-material layer, and the sticking-by-pressure lamination was carried out with an air GIAPPU 130mm sticking-by-pressure roll. Lamination speed at this time was considered as a part for 100m/. The composition of the obtained layered product is as follows. The physical properties of the laminate film (layered product) obtained 15 micrometers of nylon base-material layers, ethylene and 10 micrometers of alpha olefin copolymer-resin layers, and 30 micrometers of high-pressure-produced-polyethylene resin layers are evaluated, and the evaluation result is shown in Table 1.

[0031] Example 8 resin temperature was made into 320 degrees C, except not ozonizing, it fabricated like the example 1 and the physical properties of the obtained laminate film

(layered product) were evaluated. The evaluation result is shown in Table 1.
[0032] As the material of exam ; 9-15 and the example 3 of compariso l base-material layers. It carried out like the example 1 except having used the polyethylene-terephthalate resin (PET : diamond foil H made from diamond HOIRUHEKISUTO, Inc. 500#12 12 micrometers), and having used ethylene and 10 micrometers of alpha olefin copolymer-resin constituent layers which fabricated the pelletized resin which was blended by the blending ratio of coal shown in Table 2 as ethylene and alpha olefin copolymer resin, and which carried out melting mixture at temperature with a resin temperature of 290 degrees C in the shape of a film. The physical properties of the obtained laminate film (layered product) are evaluated, and the evaluation result is shown in Table 2.
[0033] Example 16 resin temperature was made into 320 degrees C, except not ozonizing, it fabricated like the example 9 and the physical properties of the obtained laminate film (layered product) were evaluated. The evaluation result is shown in Table 2.
[0034] The laminate film (layered product) manufactured in the example 17 example 9 was passed the speed for 100m/in the hot blast oven heated by 100 degrees C, and heat treatment was performed for about 2 seconds. The physical properties of the obtained layered product were evaluated. The evaluation result is shown in Table 2.

0037] *1: Ethylene butene-1 copolymer-resin material obtained according to the metallocene catalyst of MFR=35, density 0.885, and 23 % of the weight of butene-1 contents (C2-C4 copolymer).
*2: Ethylene butene-1 copolymer-resin material obtained according to the metallocene catalyst of MFR=4, density 0.912, and 13 % of the weight of butene-1 contents (C2-C4 copolymer).
*3: Ethylene hexene-1 copolymer-resin material obtained according to the vanadium catalyst of MFR=16, density 0.895, and 18 % of the weight of hexene -1 contents (C2-C6 copolymer).
*4: Mitsui petrochemical company make -- the ethylene butene-1 copolymer-resin material obtained according to "A20090" MFR=18 and the vanadium catalyst of density 0.895
*5: the product made from Japanese PORIKEMU -- "LC600A" MFR=7 and the low-density-polyethylene resin material (low density PE) of density 0.919